

Carbonyl Removal from Nonoxygenated Solvents

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CARBONYL COMPOUNDS in trace amounts exert a profound influence on the flavor and quality of foods and are involved in the oxidation of lipid materials. As a consequence of their importance, paper, column, and gas chromatographic techniques have been developed for the determination of microgram amounts of carbonyl compounds. In the separation of these carbonyls from their substrates large amounts of carbonyl-free solvents are required. Generally, nonoxygenated water immiscible solvents, such as hexane, benzene, and carbon tetrachloride, are used in preliminary extractions. Schwartz and Parks (2) have reported that trace amounts of carbonyls

in such solvents can be converted to their 2,4 - dinitrophenylhydrazones (DNPH's) when they are passed through a Celite column impregnated with 2,4-dinitrophenylhydrazine (DNPH), phosphoric acid, and water. Their cleanup procedure is, however, slow—approximately 1 liter in 24 hours, and requires the removal of soluble DNPH and the carbonyl derivatives from the solvent. Sulfuric acid is an efficient scavenger for most oxygenated compounds in solvents resistant to its attack. Davidow (1) used partition chromatography on Celite impregnated with sulfuric acid-fuming sulfuric acid to remove fats from DDT dissolved in carbon tetrachloride, the fat being

retained on the column. We have found that solvents, such as hexane, that are badly contaminated with carbonyl compounds may be cleaned up rapidly and continuously on a column prepared from Celite impregnated with concentrated sulfuric acid. The cleanup is quantitative, involves little or no auxiliary treatment, and is applicable to solvents commonly used in extraction procedures.

EXPERIMENTAL

Column Preparation. Sixty milliliters of concentrated sulfuric acid are added to 100 grams of Celite 545 (Johns-Manville) in a 1-liter beaker and stirred with a glass rod until a uniform blend

is obtained. The chromatographic tube is approximately 2.5×80 cm. equipped at the bottom with a coarse, fritted disk and ending in a stopcock (preferably Teflon) to control flow rate, and at the top with a female 24/40 $\frac{1}{8}$ joint to receive a solvent reservoir. Some of the solvent to be purified is poured into the column. Anhydrous granular sodium sulfate, reagent grade, is added to a depth of approximately 10 cm., and then 160 grams of the sulfuric acid-Celite adsorbent is added in portions, tamping each portion tightly before the addition of the next. This section of the column is approximately 30 cm. long. The column is topped off with 7 to 8 cm. of crystalline sodium sulfate. Flow rates of 3 to 5 ml. per minute are satisfactory.

Carbonyl compounds present in a 50-ml. aliquot of solvent both before and after purification were converted to their DNPH's. The monocarbonyl DNPH's were isolated according to the method of Schwartz and Parks (2), then dissolved in chloroform and diluted to the necessary volume for reading in the spectrophotometer. Absorbance was measured at $362 m\mu$ and corrected for dilution to correspond to the carbonyl DNPH absorbance attributable to the carbonyl concentration in the original solvent sample.

RESULTS AND DISCUSSION

Three hydrocarbon and three chlorinated hydrocarbon solvents were analyzed for their carbonyl content before

Table I. Absorbance Corrected for Blank Attributable to Aliphatic Monocarbonyl Content of Several Nonoxygenated, Water Immiscible Solvents

Absorbance measured in chloroform at $362 m\mu$.

Solvent	Absorbance	
	Before cleanup	After cleanup
CH_2Cl_2	0.06	0.002
CHCl_3	1.69	0.004
CCl_4	1.06	0.009
Hexane	1.92	0.009
Skelly F	5.64	0.000
Benzene	0.00	0.000

and after cleanup. The monocarbonyl DNPH absorbance corrected for blanks is given in Table I. The blanks are attributed to impurities present in DNPH (2). Blanks have been minimized by recrystallization and by washing the DNPH crystals with the solvent under study prior to use; nevertheless, blanks ranged in value from 0.007 absorbance unit for hexane to 0.090 absorbance unit for methylene chloride. Absorbance values of 0.02 roughly correspond, in terms of *n*-alkanals, to 1 micromole of carbonyl per liter of solvent. All solvents were essentially carbonyl-free after one pass through the column. Methylene chloride and ben-

zene contained very little carbonyl impurity prior to purification. The carbonyl impurities for the other solvents ranged from approximately 50 micromoles per liter for carbon tetrachloride to 280 micromoles per liter for Skelly F. Hexane was analyzed at frequent intervals during a 2-week period in which the purification column was in constant use and was carbonyl-free at all times. The hexane was ready for use without further treatment after passing through the column. Chloroform prior to cleanup required a preliminary water wash, followed by drying over anhydrous sodium sulfate to remove alcohol. Methylene chloride emerged from the column with a slight pink tinge. This was readily removed by shaking with a small amount of activated alumina. The column itself darkened with continued use, but the efficiency was apparently unimpaired. We have also used columns with only 50 grams of the sulfuric acid-Celite adsorbent and have obtained just as efficient results. No effort was made, however, to evaluate their period of usefulness.

LITERATURE CITED

- (1) Davidow, B., *J. Assoc. Offic. Agr. Chemists* **33**, 130 (1956).
- (2) Schwartz, D. P., Parks, O. W., *ANAL. CHEM.* **33**, 1396 (1961).